Fluorescence Spectra of Cuprous Halides at Low Temperatures

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Ikuji TSUJIKAWA and Eizô KANDA

The Research Institute for Iron, Steel and Other Metals

(Received February 25, 1954)

Synopsis

The spectrophotographs of the visible fluorescence spectra, of cuprous halides excited by cathode ray were taken at temperatures ranging from room to liquid oxygen temperature. In cuprous chloride, we observed a colour change of fluorescence, that is, green fluorescence observable at high temperatures which disappeared at about −85°C, and below this temperature red fluorescence appeared. The red band also existed at high temperatures with considerable intensity but was covered with a green band to the sense of eyes. In bromide and iodide, no considerable change was observed and only the red fluorescence appeared over a certain range of temperature.

I. Introduction

Fluorescence substances containing additional copper as an impurity for example, as ZnS/Cu phosphor frequently give green fluorescences. The flame spectrum(1) of cuprous chloride also consists of strong green band. On the other hand, some pure copper compounds, for instance, cuprous chloride and cuprous thiourea chloride, fluoresce in green. From this spectral resemblance, it seems that cuprous ion in the above three cases plays the same role in lighting phenomena.

It was formerly known(2) that cuprous chloride can fluoresce at low temperatures, and that colour change takes place between −100°C and −150°C when excited by ultraviolet rays, spectrophotographic researches, however, have not yet been undertaken. Hence, the present investigation was undertaken to study spectrographically the fluorescence spectra of cuprous chloride, bromide and iodide, and to examine the mechanism of colour change in the fluorescence of cuprous chloride at low temperatures.

II. Experimental

The apparatus in which the specimens can be struck by the cathode ray is shown in Fig. 1. It is a modified Dewar flask, a copper block being soldered to the lower end of the inner cylinder by copper-glass seal. One electrode A of disk form stands aslant against the bottom of the copper block, on

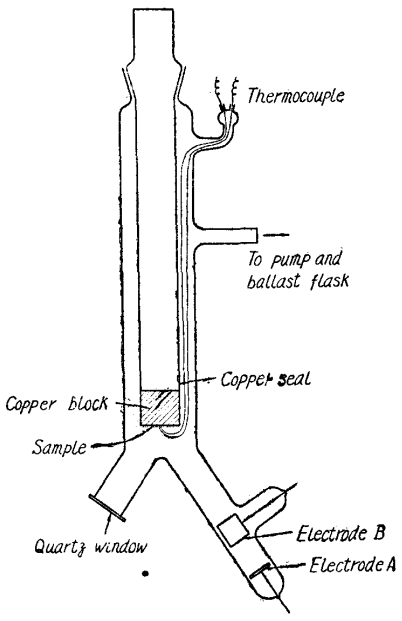

Fig. 1. Cryostat for Specimen.

* The 752nd report of the Research Institute for Iron, Steel and Other Metals.

(1) S. P. Sinha, Current Sci. (India), **17** (1948), 208.

(2) J. T. Randall, Trans. Faraday Soc., **35** (1939), 2.

the surface of which the specimen is labeled, and the other cylindrical one B is placed in the passage of electrons. Electrons emitted out of the electrode A pass through B and are projected directly on the specimen. Fluorescence light through the window is reflected horizontally by the mirror and measured with a spectrograph of two glass prisms. 15,000 volts can be applied between two electrodes by a leakage transformer. This discharge takes place at the pressure of about 10^{-2}mmHg, which can be kept stable by a ballast flask of 20 litres. The temperature of the specimen can be kept uniform by placing it horizontally.

III. Results of experiments

The total intensity of fluorescence of coprous chloride versus temperature curve is shown in Fig. 2, and its microphotometer curves of fluorescence spectra at various temperatures are shown in Fig. 3. At room temperature, it showed weak green and red fluorescent bands, and with the lowering of temperature, their intensities increased, showing a maximum at about -75°C. On further lowering of temperature their intensities decreased and almost disappeared at $-85° \pm 3$°C, and at the lower temperatures it fluoresced in red. The temperature at which this change in colour occurred was the same for both lowering and raising the temperature of the specimen. This temperature was considerably different from that measured by ultraviolet excitation which was between $-100°$ and -150°C.

The high temperature spectrum had two bands: one was green and the other red, the latter being continuously observable in the low

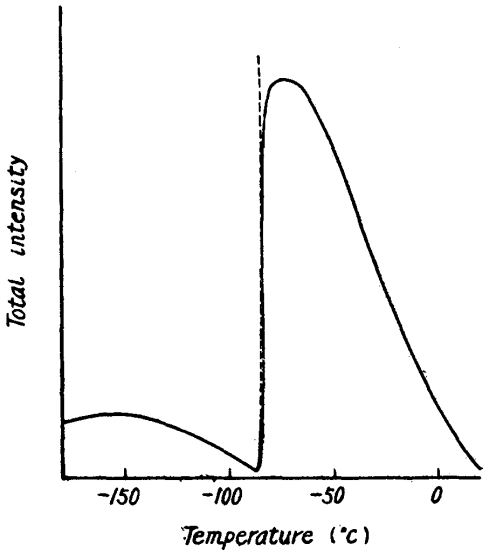

Fig. 2. Curve of total fluoresence intensity in CuCl.

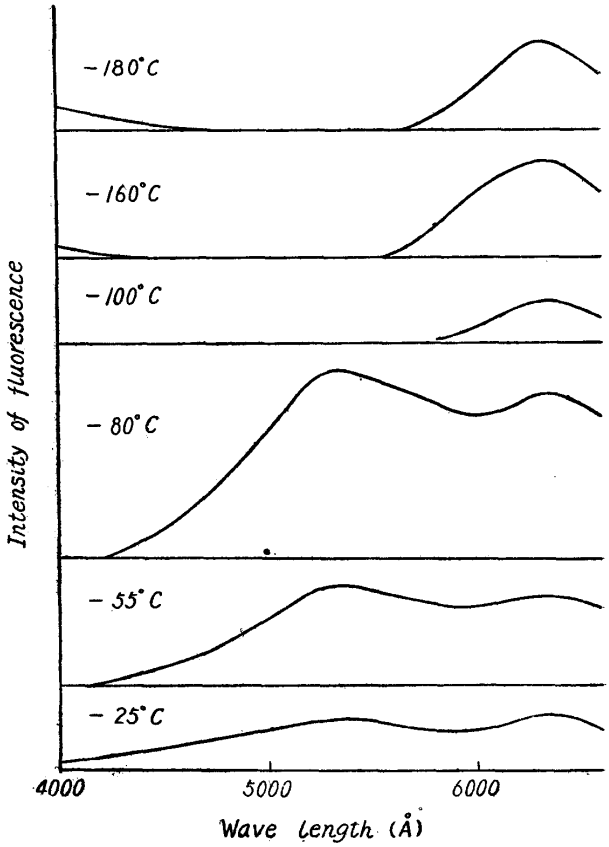

Fig. 3. Fluorescence Spectra of cuprous chloried at various temperatures.

temperature spectrum. The green band increased its intensity with the lowering of temperature, had maximum intensity at −75°C and suddenly disappeared at −85°±3°C. The red spectrum reached a maximum at about −160°C and became slightly feeble on further cooling, and the violet spectrum also appeared at about −180°C. Both cuprous chloride and bromide fluoresced in red at room temperature and the violet band also appeared with the lowering of temperature. Their intensities reached a constant maximum value at −70°C in the bromide and at −120°C in the iodide, and below these temperatures the respective intensities were kept constant till −180°C. These aspects of the low temperature spectrum were all common to cuprous halides. In the present experiment, it was impossible to increase the electron current above a certain limiting value for the purpose of shorter exposure, because the heating effect of striking electrons became superior to the cooling effect of liquid air, and if the temperature rises so high, the specimen will be blackened by its decomposition into cupric chloride and copper. In all cases there was no accumlation of light; when we excited the specimen at −180°C and raised its temperature after the excitation, no fluorescent emission was observed.

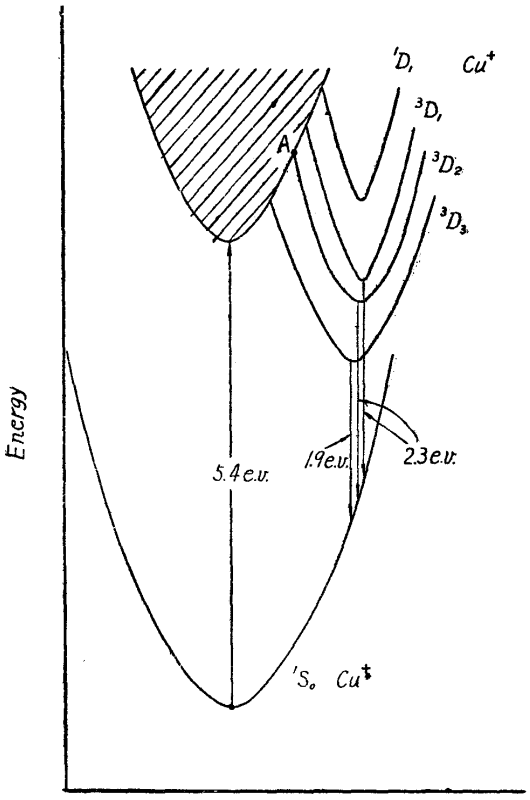

Fig. 4. Probable behaviour of electronic level of CuCl

IV. Discussion

First, we shall examine the energy levels of Cu^+ electron configuration. The green fluorescence band of cuprous chloride at high temperatures lies in the same region as that in the flame spectra and fluorescence ones of phosphor containing Cu^+ ion as impurity activator. Considering the identification of electronic levels in the cases of flame and phosphor spectra, it seems probable that the green band is due to the transition of electron from Cu^+ excited level $^3D_2$ or $^3D_1$ to the ground level $^1S_0$[3] (Fig. 4).

On the other hand, the absorption spectrum was already measured by O'Bryan and Shneider[4], who noticed three maxima at 1920, 1500 and 1300 Å. Ultraviolet light for excitation[2] was certainly shorter than 2300 Å in Randall's experiment. We also ascertained that the fluorescence could not be excited by

(3) Y. Uehara, Bull. Chem. Soc. Japan, **14** (1939), 539.
(4) G.M. Schneider and H.M. O'Bryan, Phys. Rev., **51** (1937), 293.

3650 Å and 2537 Å. In gaseous state, the excitation could be possible by light shorter than 2340 Å[5]. Thus, it seems that the excitation by the cathode ray probably corresponds to that by light shorter than 2300 Å. Furthermore, a photoconductivity was observed when irradiated by light below 2250 Å[6].

It is quite probable that the energy is absorbed by the Cu^+ ion in the perfect lattice in the case of excitation by the cathode ray, and that all Cu^+ ions contribute to emission phenomena. The possibility that electrons can be elevated to the conduction band of Cu^+ ion may be correlated with the easy occurrence of a cupric compound. We have calculated the energy for the excitation of electron from Cu^+ ion in perfect lattice to the lowest state of conduction band by the method of energy cycle[7]:

$$h\nu = I_2 - \chi + \frac{Ae^2}{r_0} + \omega + \Delta U$$

This procedure is shown in Table 1. Our calculated value 5.63eV (about 2200 Å in wavelength) almost coincides with the least energy (2300 Å) necessary for the excitation.

Table 1

	Energy in e.v.
Second ionization energy of Cu[9]	20.2
Electron affinity of crystal[10]	0.5
Madelung's energy[10][11]	10.02
Deporalization energy[12]	−5.42
Correction for covalent band[13]	1.37

The mechanism of transfer of conduction electron to the excited states of Cu^+ ion has not yet been ascertained, but we propose a possible mechanism in the case of cuprous chloride by the configuration scheme shown in Fig. 4. Concerning the colour change, as there is no structural transition in cuprous chloride[8] at about −85°C, this change should be accounted for by the electronic configuration. If conduction electrons can be elevated above the point A by thermal agitation at temperatures above −85°C, they will be transferred to the minimum position of $^3D_1$ or $^3D_2$ state and fluoresce not only in red but also in green. If, however, electrons cannot reach the point A below −85°C, only the red fluorescence will appear by transition form $^3D_3$ to the ground state. The mechanism of the colour change in the fluorescence may be explained by this model, but the mechanism of the intensity change over a range of temperature will remain a question and we shall not go into more detailed discussion until new results will be known.

This research was aided by the Scientific Research Funds of the Department of Education.

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(6) P. Lukirsky, N. Gudris and L. Kulikowa, Z. Phys., **37** (1926), 308.
(7) c.f. N.F. Mott and M.J. Littleton, Trans. Faraday Soc., **34** (1938), 485.
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(9) R.F. Bacher and S. Goudsmit, *Atomic Energy States* (1932).
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(11) R.W.G. Wyckoff and E. Posnjak, J. Am. Chem. Soc., **44** (1922), 30.
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